Faculty of Science,
University of Technology, Sydney

PhD Thesis

Optical Properties of Transition-Metal-Doped GaN and ZnO for Spintronics Applications

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Certificate of Authorship and Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

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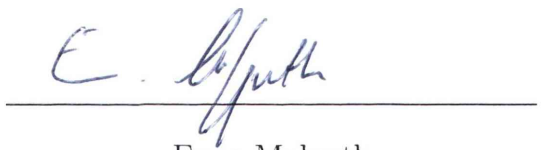

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List of publications

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E. Malguth, A. Hoffmann and X. Xu, "Internal $^5E \rightarrow {}^5T_2$ transition of Fe^{2+} in GaN," *Phys. Rev. B* **74**(16): 165201 (2006).

E. Malguth, A. Hoffmann, M. Phillips and W. Gehlhoff, "Fe-centers in GaN as candidates for spintronics applications," in "Symposium Proceedings," , (edited by M. Kuball, T. Myers, J. Redwing and T. Mukai), volume 892, 131–136, Mat. Res. Soc., Vol.892 (2006).

M. H. Kane, M. Strassburg, W. E. Fenwick, A. Asghar, J. Senawiratne, D. Azamat, E. M. Z. Hu, S. Graham, U. Perera, W. Gehlhoff, A. Hoffmann, N. Dietz, C. J. Summers and I. T. Ferguson, "Optical studies of MOCVD-grown GaN-based ferromagnetic semiconductor epilayers and devices," *physica status solidi (c)* **3**(6): 2237–2240 (2006).

O. Gelhausen, E. Malguth, M. R. Phillips, E. M. Goldys, M. Strassburg, A. Hoffmann, T. Graf, M. Gjukic and M. Stutzmann, "Doping-level-dependent optical properties of GaN:Mn," *Applied Physics Letters* **84**(22): 4514–4516 (2004).

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of Mn-doped GaN," *Mat. Res. Soc. Symp. Proc.* **798**: 569–574 (2004).

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Summary

Spin-based devices have the potential to take modern electronics and optoelectronics to the next level. So-called 'spintronics' exploit both the charge and the spin of an electron for data processing, transport and storage. A significant step towards the realisation of such devices would be to achieve room temperature ferromagnetic semiconductors. Theoretical works predict the possibility of room temperature ferromagnetism in the wide bandgap semiconductors GaN and ZnO doped with transition metals. The present models of spin-coupling in such dilute magnetic semiconductors require input in form of quantitative information on electronic states that arise from the introduction of transition metal ions into the host lattice. This work focuses on the detailed experimental investigation of such states in GaN and ZnO doped with different transition metals.

A large array of Fe, Mn and Ni doped GaN and ZnO samples with different doping levels and n-type and p-type co-doping were intensively studied by a wide range of experimental techniques. The investigation of Fe doped GaP, GaAs and InP provided valuable insights into the transient shallow acceptor state constituted by a hole bound to Fe^{2+}. The most significant results are summarised in the following:

A comprehensive literature review is presented on the Fe centre in III-V and II-VI semiconductors. Experimental and theoretical data that have been obtained over a few decades were reviewed thoroughly unveiling common phenomena that can be generalised to other TMs. The positions of established $Fe^{3+/2+}$ and $Fe^{2+/1+}$ levels were summarised allowing for predictions on the positions of further charge transfer levels based on the internal reference rule. The $Fe^{3+/4+}$ level has not been identified unambiguously in any of the studied materials. Detailed term schemes of the observed charge states in tetrahedral and trigonal crystal field symmetry are presented including fine structure, isotope effects and a dynamic Jahn-Teller effect.

By means of cathodoluminescence experiments Ni and Fe doping of HVPE-grown GaN was found to promote the formation of inhomogeneous regions with increased donor density and enhanced luminescence efficiency. In these regions richly structured cathodoluminescence patterns are observed at the surface.

By means of optical studies on high quality Fe doped GaN samples the electronic

structure of Fe^{3+} and Fe^{2+} was established in great detail. The effects of spin-orbit interaction, of the axial distortion of the crystal field in hexagonal GaN and of the Jahn-Teller coupling were successfully investigated. Both the Fe^{3+} centre and the Fe^{2+} centre were found to be stabilised against a dynamic Jahn Teller effect by the trigonal symmetry of the wurtzite lattice. A bound state with a binding energy of 50±10 meV was identified as a hydrogenic state consisting of a hole localised at an Fe^{2+} centre. This [Fe^{2+},h] state represents a transient shallow acceptor state. It could be described by effective-mass-theory revealing an effective Bohr radius of 1.5 nm which may enable a long-range spin interaction via overlapping wavefunctions at relatively low Fe doping. The position of the $Fe^{3+/2+}$ acceptor level could be narrowed down to 2.863±0.005 eV above the valence band maximum. Acting as a deep acceptor Fe incorporation was shown to quench the intrinsic yellow luminescence of GaN by lowering the Fermi level and passivating native donor states. Implications concerning the internal reference rule are discussed.

A deep understanding of the effective-mass-like state [Fe^{2+},h] could be obtained by temperature and stress dependent measurements on Fe doped GaP, GaAs and InP. Besides the ground state, the hole was observed in several excited hydrogenic states each involving different Fe^{2+} fine structure states. Particularly for the hydrogenic ground state, a weak exchange interaction was found between the hole Fe^{2+} core states. Due to finite *p-d* hybridisation of Fe orbitals with the valence band, a weaker binding energy was observed for the ground state than predicted by effective mass theory. Finally, with regard to the Fe^{3+} ground state, $^6A_1(S)$, in GaP and InP, the hyperfine structure level Γ_8 was found to be above the Γ_7 level.

ZnO:Fe samples were prepared by Fe coating ZnO crystals, which were grown from the gas phase, and subsequent annealing under varying atmospheres. In these samples the internal $Fe^{2+}(^5E—^5T_2)$ transition was observed for the first time at 395.7 meV by means of Fourier transform infrared transmission spectroscopy. This value is in good agreement with the general trend in III-V and II-VI materials that the ($^5E—^5T_2$) energy rises with an increasing degree of ionicity and decreasing lattice constant. No axial symmetry was found for the Fe^{2+} centre which is unusual for wurtzite ZnO. Possible reasons are discussed taking into account a strong Jahn-Teller effect, the non-constant c/a-ratio of ZnO and a high concentration of defects. Moreover, Fe-defect complexes and local vibrational modes could be identified.

A large array of GaN samples with varying Mn concentrations and n-type and p-type co-doping allowed for a systematic charge state tuning by shifting the Fermi level providing access to the oxidation states Mn^{2+}, Mn^{3+} and Mn^{4+}. The respective electronic structures were investigated by means of optical and magnetic techniques.

The Mn^{3+} centre and Mn^{4+} centre showed clear effects of degradation of crystal quality as a result of Mn, Si and Mg doping. A strong tendency was demonstrated for the formation of Mn-Mg complexes. A photoluminescence structure found around 1 eV in Mg co-doped GaN:Mn samples was proven to originate from Mn^{4+} involved in such complexes. A resonant Stokes process by secondary excitation and stimulated hole transfer was established in these Mn-Mg complexes. The $Mn^{3+/4+}$ donor and $Mn^{3+/2+}$ acceptor levels were found 1.15 eV and 1.65 eV above the VB maximum, respectively, compensating n-type and p-type doping. As a consequence, there is no reasonable chance to achieve high carrier concentrations in GaN:Mn, a precondition for free-carrier-mediated spin-coupling.

The results presented in this thesis contribute to the general understanding of transition-metal-related electronic states in III-V and II-VI semiconductors, particularly in GaN and ZnO. These new insights are valuable contributions to a targeted design of dilute magnetic semiconductors that will help to, one day, realise next-generation spintronic devices.

Contents

List of Symbols and Abbreviations

a_B	Bohr radius
arb. units	arbitrary units
BE	backscattered electron
BL	blue luminescence
CAS	calorimetric absorption spectroscopy
CB	conduction band
CCD	charge coupled device
CF	crystal field
CL	cathodoluminescence
CT	charge transfer
DAP	donor acceptor pair
DMS	dilute magnetic semiconductor
e	electron
E_b	binding energy
EMT	effective mass theory
EPR	electron paramagnetic resonance
ESEM	environmental scanning electron microscope
eV	electron volt
ε_0	vacuum dielectric constant
ε^*	effective dielectric constant in ε_0
FTIR	Fourier transform infrared
FWHM	full width at half maximum
Ga_i	gallium interstitial
h	hole
HJ	heterojunction
HV	high voltage
HVPE	hydride vapour phase epitaxy
IR	infrared
JT	Jahn-Teller effect

$\vec{k}$	wave vector of propagating light
LA	longitudinal acoustic
LED	light emitting diode
LO	longitudinal optical
LVM	local vibrational mode
m_0	electron mass
m_{eff}	effective mass
m^*	relative effective mass in m_0
MOCVD	metalorganic chemical vapour deposition
μ_B	Bohr magneton
pi	photoionisation
PL	photoluminescence
PLE	photoluminescence excitation
PMT	photo multiplier tube
r_B^*	effective Bohr radius
RKKY	Ruderman-Kittel-Kasuya-Yosida
SC	semiconductor
SE	secondary electron
SEM	scanning electron microscope
SIMS	Secondary ion mass spectroscopy
SO	spin-orbit interaction
SQUID	superconducting quantum interference device
σ^+	left-circularly polarised
σ^-	right-circularly polarised
T_C	Curie temperature
TA	transversal acoustic
TM	transition metal
TO	transversal optical
UV	ultraviolet
VB	valence band
Vis	visible spectral range
XRD	X-ray diffraction
YL	yellow luminescence
ZPL	zero phonon line

List of Figures

List of Tables